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UNITED STATES ATOMIC ENERGY COMMISSION

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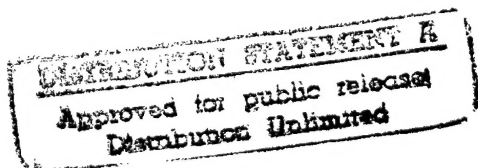
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for possible publication.

Date of Manuscript: May 28, 1948
Date Declassified: June 28, 1948

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Technical Information Branch, Oak Ridge, Tennessee
AEC, Oak Ridge, Tenn, 4-11-49--850-A1521

Printed in U.S.A.
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A NEW TECHNIQUE FOR THE DETERMINATION OF HEATS OF SUBLIMATION OF SLIGHTLY VOLATILE SUBSTANCES

By O. C. Simpson and R. J. Thorn

A technique is described which enables one to measure relative vapor pressures by measuring the rate of change of transmissivity of thin deposits as they are formed by condensation from the vapor. From the temperature dependence of this rate the heat of sublimation of slightly volatile substances can be determined. In the case of graphite, deposits of the order of $0.1 \mu\text{g per cm}^2$ can be detected.

INTRODUCTION

Two general methods of determining the heat of vaporization or sublimation are discussed. One method is based upon the measurement of the slope of the plot of $\log_{10} p$ against the reciprocal absolute temperature and requires only relative vapor pressure measurements as a function of temperature; the other, based upon the calculation of the absolute entropy difference of the vapor and the condensed phase, requires the measurement of the absolute vapor pressure at a known temperature plus a knowledge of the pertinent specific heat data. Of these methods the second is usually the more accurate, but the first one presents certain advantages since factors such as the vaporization coefficient must be rather strongly temperature dependent to cause large error and since only relative vapor pressure measurements are required. Also no specific heat data are needed.

One of the chief difficulties in the application of either method to substances having low vapor pressures, graphite for example, is that ordinary techniques for determining the small rates of evaporation require long times. The technique described in this report enables one to measure extremely small rates of evaporation (actually condensation) and hence enables one to employ the first method without employing long times. The same technique can also be used in the second method provided a proper calibration is made.

The authors are employing this technique in conjunction with the first method to determine the heat of sublimation of graphite. As yet the investigation has not been completed to the authors' satisfaction. However, others may have use for this technique and since it will be some time before the investigation is concluded, the experimental method is described here.

THEORY

The technique presented herein is essentially as follows. A fraction of the material evaporating from the top surface of a cylinder, heated in an evacuated space, is collected on a circular target placed above and parallel to the surface. The time rate of deposition of the material is determined by measuring the time rate of change of the transmissivity of the target. The light from the incandescent material serves as a light source for this measurement. At feasible temperatures for substances in which we are interested, graphite for example, the rate of deposition is so small that ordinary methods such as weighing do not permit its determination within reasonable times. However, the use of an optical pyrometer constitutes a very sensitive method for the determination of this rate. From the dependency of the deposition rate on temperature it is possible to calculate relative vapor pressures and therefrom the heat of sublimation. The experimental arrangement is represented schematically in Figure 1.

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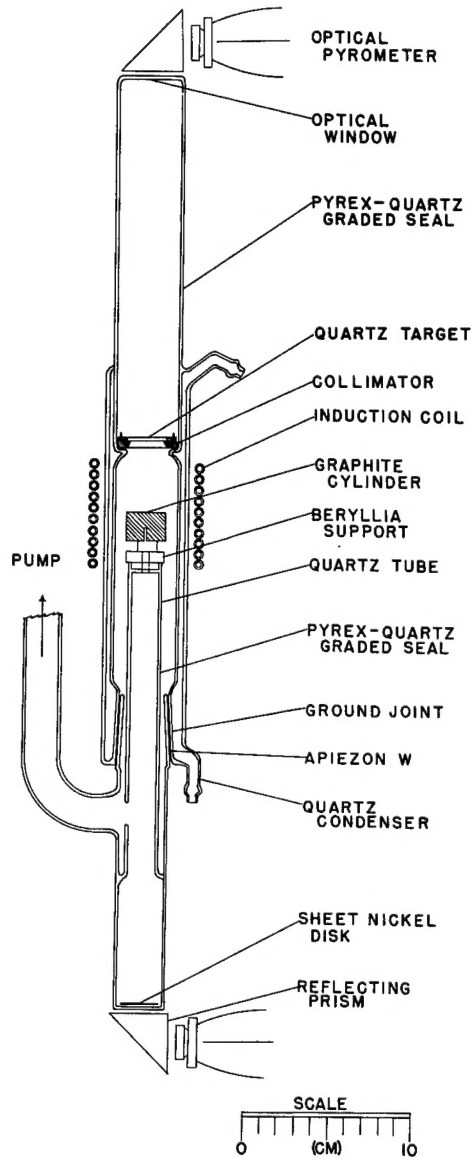


Figure 1. Experimental arrangement used to determine rate of evaporation of solids.

If light of intensity I_0 and wavelength λ emitted from the top surface of the cylinder at some high temperature $T^\circ\text{K}$ is intercepted by the layer of the material deposited on the quartz target, then the decreased intensity I of light entering the optical pyrometer is given in terms of the thickness, x , of the deposit by the relation

$$I = I_0(1 - r_1)(1 - r_2)(1 - r_3) e^{-kx - k_q x_q} \quad (1)$$

In this equation r_1 , r_2 , and r_3 are the reflectivities of the deposit-vacuum, the deposit-quartz, and the quartz-vacuum interfaces respectively; k and k_q are the absorption coefficients of the material and quartz; and x_q is the thickness of the quartz. More correctly there may be additional terms due to the window on the apparatus and a prism. These terms, however, can be omitted from this discussion, although they must be considered when it is necessary to measure the true temperature of the cylinder.

If we assume that the spectral intensity I_0 emitted from a nonblack body with a spectral emissivity e_λ is given by Wien's law,* we can write

$$I_0 = e_\lambda c_1 \lambda^{-5} e^{-c_2/\lambda T} \quad (2a)$$

Corresponding to the decreased intensity I there is some apparent absolute temperature T_a °K such that

$$I = e_\lambda c_1 \lambda^{-5} e^{-c_2/\lambda T_a} \quad (2b)$$

If equation 2b is divided by equation 2a and the expression for I/I_0 so obtained is substituted into equation 1, then an equation relating the apparent temperature T_a to the thickness and reflectivities is obtained. That is,

$$\frac{1}{T_a} = \frac{1}{T} + \frac{\lambda}{c_2} (kx + k_q x_q) - \frac{\lambda}{c_2} \ln [(1-r_1)(1-r_2)(1-r_3)] \quad (3)$$

If the thickness x of the material deposited on the quartz is increasing with time, due to molecules condensing on the target (in this discussion we are assuming that the vapor is composed of a single molecular species), the dependency of T_a on time can be found from the elementary kinetic theory relations. The result is

$$\frac{1}{T_a} = \frac{1}{T} + \frac{\lambda k_q x_q}{c_2} - \frac{\lambda}{c_2} \ln [(1-r_1)(1-r_2)(1-r_3)] + \frac{\lambda k F A_s}{c_2 D A_d} \sqrt{\frac{M}{2\pi R}} \frac{p}{\sqrt{T}} t \quad (4a)$$

In this expression F is the fraction of the molecules evaporating which condenses on an area that intercepts the light entering the pyrometer; A_s is the area of the top surface of the cylinder, A_d is the area of the deposit through which light passes to the pyrometer; D is the density of the deposit; M is its molecular weight; R is the molal gas constant; p is the vapor pressure of the material; and t is the time. In the derivation of this equation there is the inherent fact that when $t = 0$, r_1 is zero and $r_2 = r_3$, since no deposit is present on the target. For very small values of t , r_2 becomes different from r_3 and r_1 becomes greater than zero, but neither is necessarily independent of t (i.e., x), because the reflection of light takes place not only from the outer atomic layer but also from a finite number of atomic layers. However, for sufficiently large values of t these reflectivities become constant since the deposit is then sufficiently thick to permit the maximum reflection characteristic of the interfaces. Hence for values of t greater than this minimum and for constant values of the temperature of the cylinder, equation 4a assumes the form

$$\frac{1}{T_a} = A_0 + \frac{A_1 p t}{\sqrt{T}} \quad (4b)$$

This relation shows that the reciprocal of the apparent absolute temperature is, under the conditions already specified, a linear function of time with a slope,

$$a = \frac{\lambda k F A_s}{c_2 D A_d} \sqrt{\frac{M}{2\pi R}} \frac{p}{\sqrt{T}} \quad (5)$$

Since the Clausius-Clapeyron equation,

$$\frac{dp}{dT} = \frac{\Delta H}{T \Delta V} \quad (6)$$

* For $\lambda = 0.665$ and $T = 2500^\circ\text{K}$, $e^{-c_2/\lambda T} = 5.5 \times 10^3$. Hence one is justified in using Wien's law rather than Planck's. Whether Wien's law is strictly applicable to nonblack bodies, however, is another question which will not be discussed.

can be expressed in a form involving the derivative of the logarithm of the vapor pressure, determination of the temperature rate of change of a quantity that is proportional to the vapor pressure such as the slope a in the present case is sufficient for the determination of the heat of sublimation. Equation 6 can be expressed in the desired form by neglecting the volume of the solid phase compared with the gaseous phase and assuming the latter to be a perfect gas. If the value of p given by equation 5 is then substituted in this relation, we find

$$\frac{d \ln (a \sqrt{T})}{d(\frac{1}{T})} = -\frac{\Delta H}{R} \quad (7)$$

Hence the heat of sublimation is equal to 4.575 times the slope of the plot of $\log_{10}(a \sqrt{T})$ vs $1/T$.

Provided the absorption coefficient can be evaluated, then the technique described herein can be used to determine the absolute vapor pressure of the material at a given temperature (see equation 5). From this the heat of sublimation can be calculated according to statistical mechanical relations.*

EXPERIMENTAL EXAMINATION OF TECHNIQUE

Typical examples of the plot of the reciprocal apparent absolute temperature T_a measured through graphite deposits as a function of the time are given in Figure 2. These curves are characterized by a slight negative curvature in the initial region which becomes less with increasing time until the curve finally becomes linear. The length of the nonlinear region depends upon the temperature of the cylinder, increasing with decreasing temperature. This initial curvature is to be expected according to equation 4a, since during this period the reflectivities r_1 and r_2 are time dependent and are changing in such a manner as to make

$$\frac{d \ln [(1 - r_1)(1 - r_2)]}{dt}$$

a negative quantity that decreases numerically to zero at r_1 and r_2 constant. Hence $1/T_a$ vs time has a negative curvature until r_1 and r_2 become constant. The possibility of this nonlinear region having an effect on the calculated slope a can be excluded in two ways. In one procedure the slope of only the linear region is calculated, this region being defined as follows. If t_1 is the minimum time, which for all practical purposes is necessary for the attainment of the linear region at some temperature T_1 , then the equivalent time t_2 necessary at some other temperature T_2 can be found to be

$$t_2 = t_1 \sqrt{\frac{T_2}{T_1}} e^{-(H/R)(1/T_2) - (1/T_1)} \quad (8)$$

Since the linear region is readily discernible at the high temperature end of the permissible range, one of these runs can be selected arbitrarily for estimating t_1 . The corresponding t 's for other temperatures can then be calculated with the aid of this equation provided a rough estimate of ΔH has been made. Since accurate values of the t 's are not required, ΔH can be estimated by considering $1/T_a$ vs t to be linear for all values of t . In essence this procedure is equivalent to selecting regions of equivalent thickness. Another procedure of eliminating the initial region is by an initial deposit at a relatively high temperature before measurements of T_a vs time are made. When this procedure is used $1/T_a$ is linear in time.

The deposits whose transmissivities are represented in Figure 2 range in total weight from 23.7 μg at 2252°K to 143 μg at 2433°K for an area of about 3 cm^2 . Since one can readily read a temperature difference of 3° with an optical pyrometer, the limit of detection of the presence of the deposit is 0.11 μg per cm^2 . This corresponds to a thickness of about 5×10^{-8} or about three or four

*K. K. Kelley, U. S. Bur. Mines, Bull. 383 (1935).

atomic layers. This conclusion agrees with that of Estermann and Stern,* who found that deposits of two or three molecules in thickness are visible because of aggregation. The thickness of the graphite at which the curvature becomes zero or at which the reflectivities become constant is about 3.6×10^{-6} cm or about 250 atomic layers.

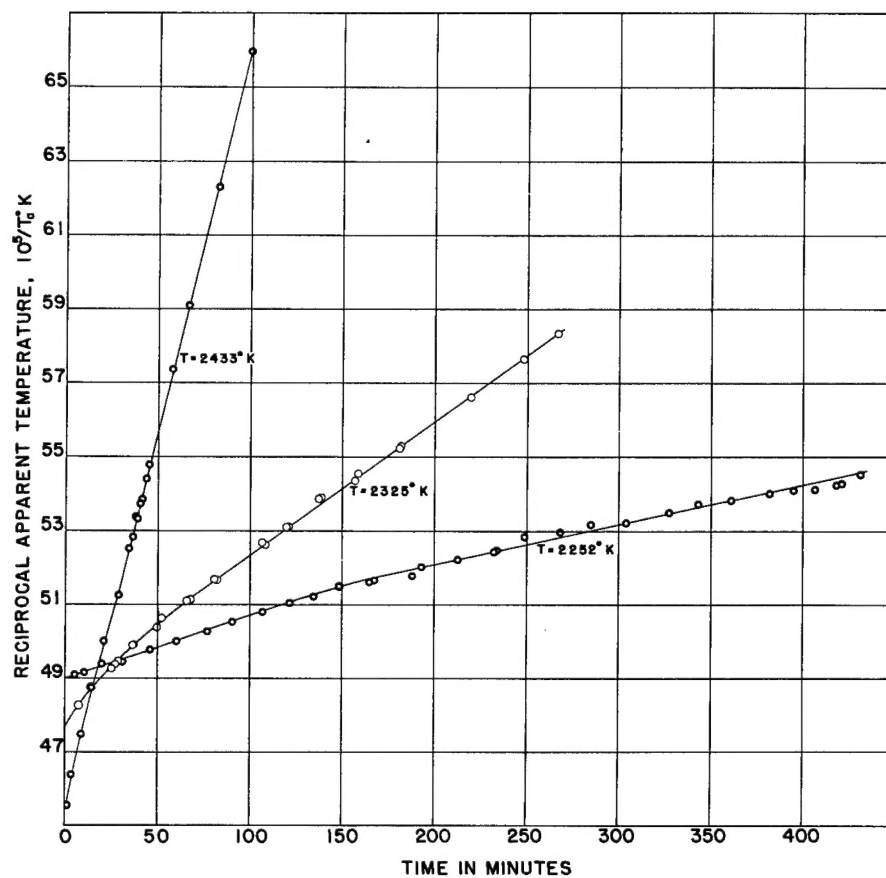


Figure 2. Relative rates of deposition of graphite.

* Estermann and O. Stern, Z. Physikal Chem. 106:399 (1923).

POSSIBLE ERRORS

The possible sources of error, which may be considered as being inherent in the transmissivity technique, are (1) the dependency of the absorption coefficient on thickness and (2) on temperature, (3) the deviation of nonblack body radiation from Wien's law, (4) thermal expansion of the deposit, and (5) the radiation from the deposit.

In general the effect of factors (1) and (3) if operative would be to make $1/T_d$ other than a linear function of time. Since we have observed a linear dependence with graphite aside from the initial effect of reflectivities, we conclude that these factors cause no error in this case unless a fortuitous combination of them causes effective cancellation. It is doubtful that the absorption coefficient of graphite changes sufficiently with temperature to cause any error since the transmissivity curve of thin graphite deposits as a function of wavelength shows no absorption peaks in the neighborhood of 0.665μ . The thermal expansion of graphite would cause $\log \sqrt{T}$ to change by less than 0.02% for the temperature range given in Figure 2. If the deposit on the quartz target emits radiant energy and if this energy were of the same order as that from the cylinder transmitted through the deposit, then values of a will be in error. However, the ratio of these intensities is $e^{-c_2/\lambda T_d} / \tau e^{-c_2/\lambda T}$ in which T_d is the temperature of the deposit and τ its transmissivity. Crude measurements showed that $\tau \cong 0.01$ (for the thickest deposit) and $T_d \cong 1000^\circ\text{C}$. Hence for the ratio we obtain 8×10^{-4} at $T = 2200^\circ\text{K}$ showing that the amount of radiant energy emitted by the deposit is negligible in our experiments compared with that transmitted from the cylinder.

The sources of error, which are not necessarily inherent in the transmissivity method but which may be present under the conditions of the experimental procedure, are (1) temperature gradients in the material, (2) variation of the vaporization coefficient with temperature, and (3) variation of the condensation coefficient with temperature. For metals temperature gradients will usually cause no trouble since their thermal conductivities are high and temperatures above 2000°K are not usually required. However, at temperatures above 2000°C these gradients become appreciable, especially in the case of graphite, and they must be taken into consideration by calculation of an "average" temperature. One of the best ways of eliminating the variation of the vaporization and condensation coefficients with temperature is to employ conditions such that they are unity. With the vaporization coefficient this can be assured if the material is vaporized in a small furnace cavity and permitted to effuse through an orifice in the furnace. In all probability the vaporization coefficient will also be unity if the surface of the material is chemically clean. With the condensation coefficient a value of unity can be approached by employing a water-cooled target.

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